Vitrification and Recycling of Hazardous Waste by Susceptor Induction Melting System

著者	PARK JONG - SOO
号	5
学位授与番号	30
URL	http://hdl.handle.net/10097/37981

	PARK JONG-SOO
氏名	朴　鍾　守
授与学位	博士（環境科学）
学位記番号	環博第３０号
学位授与年月日	平成20年3月25日
学位授与の根拠法規	学位規則第4条第1項
研究科，専攻の名称	東北大学大学院環境科学研究科（博士課程）環境科学専攻
学位論文題目	Vitrification and Recycling of Hazardous Waste by Susceptor Induction Melting System（サセプタ式高周波誘導加熱炉による有害廃棄物のガラス化とリサイクルに関する研究）
指導教員	東北大学教授　谷口　尚司
論文審査委員	主査　東北大学教授　長坂　徹也　　東北大学教授　藤崎　敬介　東北大学准教授　前川　英己

論文内容要旨

Any type of waste which contains properties that could make it harmful to the environment or human health may be classed as hazardous waste. It is not a secret to anyone that hazardous waste can become a huge problem if not dealt with appropriately. However, several decades ago, human did not give much attention into managing hazardous waste. They would just go wherever the needed resources were located in, pick it up, dump their toxic wastes and go again to the other site. This was pretty good for them at the beginning, but as the effects of the hazardous wastes in the environment gradually showed up, the world realized that something was wrong. Environmental issues caused by the hazardous wastes differ from strange diseases on human and animals to killing them; it is extremely difficult, expensive, and dangerous to clean up.

Vitrification of the waste has recently been considered as a new strategy in many countries, which is a process by which energy is applied to a material to create a molten or molten like state. This method is a proven technique in the disposal and long-term storage of nuclear waste or other hazardous wastes. The final waste form is similar to obsidian and is a non-leaching, durable material that effectively traps the waste inside. Like the other preceding processes, vitrification technique has some disadvantage, which is high economic cost due to the consumption of excessive energy.

A key to economical development of industrial vitrification processes to make wastes inert is the subsequent use of the produced glass to fabricate high-value products. Conveniently, glass is a very versatile material and allows producing a wide range of products suitable for various applications. The use of waste-derived glass in a mass market application is highly attractive since it would enable the safe, economical disposal of a large quantity of waste. In another manner, an advanced thermal-melting system can also give an economical advantage to the vitrification treatment.

There were many reports relative to induction-melting system, or vitrification, for the waste treatment.

However, these works has shown a leaning toward only one research area because researchers have been roughly divided into two groups, which are electromagnetics and ceramics. The former focused just on numerical modeling without respect to the handling of the melt and final products. On the other hand, the latter's interests were exclusively laid only on vitrifying the waste, regardless of the state of the melting system and economic charge. In addition, they did not propose yet a proper method for recycling which added economical benefits by mass consumption. Of course, there were many approaches toward the fabrication of glass-based products from the waste. But it should be noted that most of the technologies had only been demonstrated in the laboratory; to the authors' knowledge, there are rarely pilot, or plant scale applications of the technologies.

The objective of this study is the establishment of basic understanding about induction heating with the susceptor and development of technological tools to be able to safely vitrify hazardous waste into glass-like materials. Also, in consideration of recycling, the mechanical, chemical and thermal properties of inert vitreous products were investigated. A particular attention was paid to the leaching characteristics of heavy-metal ions from glasses. Thus, this thesis consists of four main parts, as the following:

1. Joule-heat generation in susceptor by induction heating
2. Numerical modeling of molten glass in induction furnace
3. Destruction and vitrification of asbestos-containing wastes (ACWs)
4. Fabrication of alkali borosilicate glass from coal fly ash

For developing a new technological tool on waste vitrification, an induction furnace was introduced along with a susceptor capturing electromagnetic energy very well. Initially, the effect of the susceptor shape on Joule heat was evaluated with the conversion of the cylinder to a tube (hollow cylinder). In the case of the stainless-steel susceptor (Φ50 mm × 80 mm), the maximum Joule heat (5.2×10^{-2} W/A^2) was generated at t/δ (tube thickness/skin depth) of 0.1 and was approximately 3.6 times higher than that of the cylinder-type susceptor. As the thickness decreases, the total induced current decreases, whereas the electric resistance shows a countertrend. The total induced current has a slope change at a certain thickness ($<\delta$) which corresponded to the thickness of maximum Joule heat. The thickness where the slope of the total induced current changes is a point minimizing the inductive reactance in the susceptor. We defined this point as a critical thickness, t_c. In conclusion, it becomes clear that the Joule heat is dependent upon three factors: skin effect, electric resistance and inductive reactance. With the decrease in the thickness to the skin depth, the Joule heat is almost constant due to the skin effect. However, from the skin depth to the critical thickness, Joule heat dramatically increases: it can be explained as the following: Joule heat = I^2R; the decrease in inductive reactance results in restraint of the decrease in the total induced current; the decrease in cross-section increases electric resistance. Namely, the induced currents are concentrated on a smaller cross-section. Finally, inductive reactance does not give a strong effect under the critical thickness. As a result, the sudden decrease in the total induced current weakens the Joule heat. Therefore, the Joule heat showed a maximum value at the critical thickness. The t/δ-dependent Joule heat values for different materials showed that if two susceptors have the same dimensions, both the maximum Joule heats have approximately the same values at the critical thickness, independent of the properties of the material. This meant that all materials could have the Joule heat similar to graphite when the tubular susceptor has the critical thickness in the same magnetic field. Eventually, the dimensionless critical thickness $(t/\delta)_c$ is merely induced as the inverse number of the dimensionless radius (r/δ, external radius/skin depth). That is, the critical thickness is determined from the skin depth and the external radius of the susceptor in the coil turns. At the critical thickness, the energy efficiencies have large and similar values (~84%) independent of the properties of material. Consequently, the applicability of the induction susceptor furnace as an energy-efficient furnace was proved.

As abovementioned, tubular susceptor can capture electric energy higher than 80 % of the coil currents and convert it into heat energy to melt wastes. But it is not all for high energy efficiency for induction furnace because heat transfer from the susceptor into molten glass remains unknown. Improved energy efficiency could come from considering energy transfer from the susceptor to molten glass as well as from the induction coil to the susceptor. Then, numerical analysis on thermal, fluid-dynamic and electromagnetic field in glass bath molten by the susceptor induction heating were carried out. Two susceptor inductions (tube-susceptor in internal heating and crucible-susceptor in external heating) were considered for a comparison on energy conservation. Also, the molten glass stirred mechanically by the tube-susceptor was modeled. The tube-susceptor induction showed higher thermal profiles than the crucible-susceptor induction under all transfer conditions: in natural convection at 2 kW (Joule heat), the tube-susceptor induction had the maximum temperature of 1950 K and average temperature of 1790 K; and the crucible-susceptor induction had the maximum temperature of 1690 K and average temperature of 1590 K. By two-dimensional velocity data model, the violent stirring in the molten glass was required for satisfactory thermal uniformity. Its results suggested that it should be simulated on three-dimensional turbulent flow. Consequently, although new challenges increased at end of this study, this simulation clearly proved that the tube-susceptor induction was an extremely useful tool available on induction furnace for vitrification.

As the first state for a new system application, Asbestos-Containing Wastes (ACWs) were transformed into glass-like materials. Asbestos is typically a very thin fiber, invisible to the naked eye (<3 μm in diameter) - for comparison, human hair is about 60 μm in diameter. If the fibrous particles are inhaled, it can cause very serious diseases such as asbestosis, lung cancer, and mesothelioma; the fibers with an aspect ratio (length/diameter) greater than 10:1 have significant carcinogenic properties. The exposure to it is mostly caused by asbestos released from the asbestos-containing wastes (ACWs). The induction furnace was combined with various conductive susceptors (Φ50 mm × 80 mm, SUS 310S) in the form of a crucible, cylinder, and tube. Their respective Joule heats generated by a coil alternating current (1 A (max), 30 kHz) were 1.25×10^{-2}, 1.35×10^{-2}, and 4.86×10^{-2} W. The energy efficiency increases up to approximately 84% when the tube susceptor is used. This is because of the decrease in the ratio of the reactive power due to the reduction of the inductive reactance between the induced currents in the susceptor. The results of field emission-transmission electron microscopy (FE-TEM) and X-ray diffraction (XRD) proved that such glasses ensured safety against the risk of exposure to fibrous asbestos. The XRD patterns also show that most of the asbestos existed in form of amosite, which has high iron content. In the recycling of ACW glasses, the addition of an appropriate reagent is necessary to improve the strength and to decrease the melting point; a change in the glass properties was accomplished by the addition of the reagents (SiO_2, B_2O_3, and $Na_2B_4O_7$). The glasses were prepared by melting the synthesized ACWs with the desired amount of the additive in an alumina crucible at 1300 °C for 30 min in order to ensure complete melting. .

ACW glasses with additives (SiO_2, B_2O_3, and $Na_2B_4O_7$) had a Vickers microhardness of 6300–7400 MPa and a fracture toughness of 0.9–1.7 MN · $m^{-3/2}$. Furthermore, the melting temperature remarkably decreased from 1210 °C to 1000 °C by the addition of 30 wt.% $Na_2B_4O_7$.

Fly ash generally contains various heavy metals which are toxic and dangerous to human beings and an ecosystem. On the other hand, alkali borosilicate glass has been noticed in glass industry because of its good mechanical, chemical properties. Therefore, as a new approach for its stabilization and recycling, alkali borosilicate glass was produced by vitrifying fly ash with the additions of Na_2O and B_2O_3. The mixtures were melted by heating them at 1500 for 30 min in an alumina crucible. The melts were poured onto a copper plate in air and allowed to solidify, thus forming a glass. The glasses so formed were then annealed at 650 for 1 h and slowly cooled down to room temperature. Glasses can be formed by fly ash with the addition of Na_2O up to 60 wt.%. With an increase in the wt.% of a glass modifier, the color of a glass changed to light green with Na_2O and to light brown with B_2O_3. Ultimately, reagent content in the glass was determined at 30 wt.% by considering the viscosity as well as the melting point. The density of the fly ash glasses decreased as the amount of B_2O_3 addition increased; this is because the density of B_2O_3 glass (1.812-1.84 g/cm^3) was lower than that of 30 wt.% Na_2O + 70 wt.% fly ash glass (2.55 g/cm^3). The Vickers microhardness in the borosilicate glasses with fly ash Initially increased with the B_2O_3 content and reached 4030 MPa at 15 wt.% B_2O_3 + 15 wt.% Na_2O. This value was comparable to window glass and Corning Pyrex® (7740) (~4100MPa). However, with a further increase in the B_2O_3 content, it decreased and attained the minimum value of 2800Mpa at 25 wt.% B_2O_3 + 5 wt.% Na_2O. The bending strength for the fly ash glasses were found to be approximately half to that for common window glass (~80 MPa). The density of material is mostly the simplest physical property that can predict mechanical strength. Conventional ceramic materials have low mechanical strength if poor density, or otherwise if high density. However, the microhardness of glasses produced in this work did not decrease with the decrease in density. Furthermore, the decrease in density is maximal when the B_2O_3 content increased from 15 wt.% to 20 wt.% (instead of the almost linear change with composition found in other glass). This is because the alkali ion Na^+ modifies borosilicate oxide glass in one of the following two ways: it changes the coordination state of boron from 3 to 4 (boron anomaly); or it creates non-bridging oxygen (NBO). The changes in Vickers microhardness can be explained from a viewpoint of the addition of Na_2O. Initially, the addition of Na_2O allowed the B atoms to be in BO_4 configuration. It also decreased the NBOs of the silicon. These explain the initial increase in the microhardness with the B_2O_3 content. However, with a further addition of Na_2O, the NBOs increased in the glass matrix. It caused the large increase of density from 5 wt.% to 15 wt.% Na_2O. In other words, this explains the observed decrease in the microhardness from 15 wt.% to 25 wt.% B_2O_3. It was proved clearly by a NMR spectroscopy. In fly ash glasses with the additions larger than 1.0 of Na_2O/B_2O_3, boron atoms more than 50 % were in 4-coordination state (BO_4), which provided the strong network connectivity to a glass matrix. Finally, their chemical resistance showed the tendency similar to that of Vickers microhardness. In the leaching test, heavy metals in fly ash were immobilized well under environmental regulation. As a result, the alkali borosilicate glass from fly ash showed the possibility for new value-added creation of by-products.

論文審査結果の要旨

わが国の石炭火力発電所から副生される石炭灰は、その75%がセメント原料に充てられているが、公共事業の縮小によりセメントの需要は減退しており、新たな利用先の開拓が求められている。石炭灰は嵩密度が小さく有害な重金属を含むため、ガラス化して減容化し、かつ重金属を封じ込めることが、最終処分あるいは利材化に有効である。また近年、アスベストによる肺がんや中皮腫などの健康被害が社会問題となっており、アスベスト含有廃棄物(ACWs)の安全な処理方法の確立が急務になっている。ACWsの無害化には溶融処理が最も有効と考えられているが、高融点かつ低熱伝導率というアスベストが有する優れた特徴が溶融処理の妨げになっている。本論文は、石炭灰およびACWsの溶融ガラス化に適した高周波誘導溶融法と、生成するガラスのリサイクルに関する研究結果をまとめたもので、全編7章よりなる。

第1章は緒論であり、本研究の背景と目的について述べている。

第2章では、本研究に関連する既往の研究を、有害廃棄物の処理方法、ガラス化処理の位置付け、誘導加熱・溶解法の原理、電磁場および熱流動場に関する数学的モデルの4つに分類して述べている。

第3章では、本研究によって開発されたサセプタ式誘導加熱炉の原理と性能について検討している。本法は、被加熱物内に装入した導電性のサセプタを電磁加熱し、内部から被加熱物を加熱溶融する方法であるが、サセプタの形状を管状にしてその肉厚を調整することによって最大のジュール発熱量が得られる条件があることを、理論的・実験的に明らかにしている。

第4章では、サセプタから発生するジュール熱の溶融ガラスへの伝熱特性を、数値シミュレーションによって解明している。溶融ガラスには温度差による自然対流が発生するが、サセプタに攪拌機能を付与することによって、より均一な温度分布が得られることを示している。

第5章では、サセプタ式誘導加熱炉を用いてACWsの溶融試験を行い、生成するガラスの特性について検討している。ACWsは1300℃で溶融し、アスベストの繊維状の形状が完全に消失してガラス化することを確認した。また、ACWsへのSiO_2, B_2O_7, $Na_2B_4O_7$の添加により、融点およびガラスの強度が大きく変化することを見出した。融点は30mass%の$Na_2B_4O_7$の添加によって1100℃まで低下させることができた。

第6章では、石炭灰にNa_2OとB_2O_3を添加して誘導溶融して得たガラスについて、密度、ビッカース硬度、曲げ強度、および有害成分の浸出特性を検討している。2種の添加物の総量を30wt%に固定して、その割合を変化させると、Na_2Oが15%では市販のアルカリ硼珪酸ガラスと同等の強度を示すが、15%を超えると強度と密度が急に低下する現象を見出した。

第7章は総括である。

以上要するに、本論文は石炭灰およびアスベスト含有廃棄物を溶融・ガラス化するための、サセプタ式誘導溶融法を新たに開発し、その加熱特性、生成するガラスの機械的特性および無害化の効果について明らかにしたもので、有害廃棄物の無害化とリサイクルの進展に寄与するところが少なくない。

よって，本論文は博士(環境科学)の学位論文として合格と認める。